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Heterogeneous Photocatalytic Oxidation of Acetone for Air Purification by Near UV-Irradiated Titanium Dioxide

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ABSTRACT

This work presents a photocatalysis-based method to treat and purify air because of its broad applicability to common, oxidizable air contaminants. The effect of oxygen content, temperature, water vapor, and acetone concentration on the photooxidation of acetone on TiO2 surface was investigated. The photocatalytic decomposition reaction of acetone obeyed the first-order equation. The decomposition rate increased with increasing the oxygen content. The rate of acetone oxidation increased when water vapor increased from 18.7 to 417 m³ and decreased at higher than 417 m³. The conversion and mineralization of acetone decreased at higher than 138 °C. The initial rate of acetone degradation can be well described by the Langmuir–Hinshelwood rate form. The specific reaction rate constant and the equilibrium adsorption are 15.8 μM/min and 0.0671 L/m³, respectively. The difference between observed and estimated half-lives became larger when the initial concentration of acetone was increased. It is

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assumed that the intermediates competed with parent compound so that delayed the half-life. The detection of CO₂ production can support this assumption.

**Key Words:** Acetone; Photocatalysis; Titanium dioxide; Langmuir–Hinshelwood equation; Kinetics; Intermediate competition.

**INTRODUCTION**

The photocatalyzed oxidative removal of trace contaminants from air is a growing research area. Attractive advantages are that this process operation at ambient temperature and pressure, use of molecular oxygen as the oxidant and final oxidation products that are usually innocuous. The photocatalytic oxidation of single compound feeds has been previously demonstrated for alkanes,[1] alkenes,[2] alcohols,[3–6] ketone,[7–10] aromatics,[10–12] halogenates,[13–15] and inorganics.[16]

Volatile organic compounds (VOCs) containing organic carbon can be vaporized at significant rates. Some are toxic and carcinogenic, and are regulated individually as hazardous pollutants. The serious problem related to the emission of VOCs is that they participate in the photochemical reaction and also in the formation of photochemical oxidants; for example, ozone and peroxyacetyl nitrate.[17]

Acetone is a common chemical used extensively in a variety of industrial and domestic application. For example, the printing industry and analytical laboratories use frequently acetone as a solvent; it is a principal constituent of many common household chemicals.[18] Very high concentration of acetone has been detected in indoor and outdoor air environment.[19] Photocatalytic oxidation of gaseous acetone was discussed recently.[7–10,18,20–22] Peral and Ollis[10] reported that the rate of acetone oxidation follows the Langmuir–Hinshelwood equation. No reaction intermediates were detected for acetone oxidation at conversions of 5–20%. Other studies[9,18,24] also showed that no reaction intermediates were observed in those experiments. In contrast, Larson et al.[25] reported the generation of a surface intermediate before complete acetone oxidation. Xu and Raftery[22] used in situ solid-state nuclear magnetic resonance spectroscopy to study acetone of photocatalytic oxidation. The surface intermediates included diacetone alcohol, mesityl oxide, formic acid, propylene oxide, and acetic acid. In a batch photo-reactor, the water vapor inhibited the degradation of acetone from 0 to 0.75 mol/m³.[23] In addition, temperature is a key parameter for the oxidation of organic vapors. The rate of acetone oxidation in the photocatalytic system can reach a maximum value at 80°C. A variation of the photocatalyst color with temperature has also been observed. After the operation at 120°C, the color was yellow, and became brown when the reaction temperature is 163°C.[26] Vorontsov et al.[8] also observed that the rate of the acetone oxidation reached a peak at about 100°C.

However, the literatures mentioned above did not use the CO₂ production to evaluate the mineralization efficiency. In this study, therefore, a batch reactor under UV light was applied for the photocatalytic degradation rate as a function of the
initial concentration of acetone, water vapor, temperature, and oxygen content. A thin film of TiO2 was coated on the internal surface of a glass tube where carried out the photocatalytic reaction. The kinetic of photocatalytic degradation of acetone in the gas-phase on TiO2 was investigated in detail. The disappearance kinetic of acetone was corresponded with a pseudo-first-order equation. The Langmuir–Hinshelwood kinetic was used to describe the heterogeneous gas-solid reaction.

MATERIALS AND METHODS

A batch reactor made of Pyrex glass is represented in Fig. 1. The annular reactor was fabricated from glass. The width of the annulus was 15 mm to 18.5 mm and the length was 300 mm. The total volume of reactor was 110 cm$^3$. Illumination was provided by a 10 W black light lamp (Sankyo Denki Japan-BLB) with a maximum light intensity output at 365 nm. Acetone and water were draw by syringes to stainless steel tube and wrapped with heating tape for vaporization. The concentration of acetone and water were controlled by the syringe pumps (KD Scientific, Model 250). The mass flow controller (MKS, Model 247C) controlled the flow rate of nitrogen and oxygen. The reactor was wrapped with heating tape to maintain the temperature of reaction.

TiO2 powder was obtained from Degussa (P-25) with a primary particle diameter of 30 nm, a crystal structure of primarily anatase and a surface area of 50 \pm 15 m^2/g (BET). The catalyst was used without pretreatment. The TiO2 was coated on the outer surface of inner tube using a well mixed slurry of 10 wt% TiO2 in deionized water. The area of catalyst film was 52 cm$^2$. The TiO2-coated tube was heated at 110°C for 1.5 h.

A typical experiment followed the steps. First, closed the valves at the two side of reactor if the concentration of acetone stabilized. Additionally, turned on the

![Figure 1. Setup of experimental apparatus. 1. N2 cylinder; 2. O2 cylinder; 3. mass flow controller; 4. syringe—acetone; 5. syringe—water; 6. mixer; 7. detector of dewpoint; 8. valve; 9. photocatalytic reactor; 10. sampling pore; 11. temperature controller.](image-url)
UV lamp then turned off the lamp after one minute. Whereas, inserted a 20mL syringe into sampling pore to adequately mix the gas in the reactor. Then, used gastight syringe to sample from the sampling pore. Finally, repeated step 2–4 until the reaction completed.

Reaction samples were analyzed by a China GC-9800F gas chromatograph equipped with a flame ionization detector (FID). A porapak Q packed column (1 m long × 1/8 inch o.d.) was employed to analyze the concentration of acetone. Nitrogen was used as the carrier gas. Carbon dioxide formed as a result of acetone photooxidation was analyzed with an FID and a porapak N column (2 m long × 1/8 inch o.d.) after converting CO$_2$ to CH$_4$ through a Ni-catalyst methanizer. The temperature of porapak N column and methanizer was 60°C and 370°C, respectively.

RESULTS AND DISCUSSION

Effect of Initial Concentration

The effect of initial acetone concentration on degradation rate is exemplified by Fig. 2 when temperature was 138°C, oxygen content was 20%, and water vapor was 18.7 μM. The remaining concentration is a function of the reaction time. The photocatalytic decomposition reaction follows a first-order expression (Eq. (1)).

$$ r = -\frac{dC}{dt} = k_{\text{app}}C $$

where $r$ is the reaction rate for the oxidation of acetone, $C$ is the concentration of acetone at the reaction time (t) and $k_{\text{app}}$ is the apparent rate constant.

![Figure 2](image-url)
The integrated form of Eq. (1) is

\[ -\ln \frac{C}{C_0} = k_{\text{app}} t \]  

(2)

This relationship between \( -\ln (C/C_0) \) and reaction time is linear. The slope of the line is the apparent rate constant, \( k_{\text{app}} \), shown in Fig. 3. Table 1 lists \( k_{\text{app}} \), initial reaction rate \( (r) \) and half-life values \( (t_{1/2}) \) of the photodegradation of acetone as a function of initial concentration. It is obvious that the rate increased with increasing initial concentration of acetone. The rate of photocatalytic oxidation was controlled by adsorption of reactant and desorption of product. The adsorption of reactant was the limiting-rate step at low concentration. Increasing the concentration of acetone increased the adsorption of reactant on TiO\(_2\) surface. Hence, the oxidation rate increased with increasing the concentration of acetone. On the other hand, the amount of adsorption was limited by adsorption site on TiO\(_2\) surface. Increasing the concentration of acetone could not add the amount of adsorption at high concentration. Desorption of product became the limiting-rate step.

### Table 1.
Comparison of apparent rate constants \( k_{\text{app}} \), \( t_{1/2} \), and \( t_{1/2} \) for the photodegradation of acetone at different initial concentrations.

<table>
<thead>
<tr>
<th>( C_i ) (( \mu )M)</th>
<th>( k_{\text{app}} ) (1/min)</th>
<th>( r ) (( \mu )M/min)</th>
<th>( t_{1/2} ) (min)</th>
<th>( t_{1/2} ) (min)</th>
<th>Mole of CO(_2) produced/mole of acetone degraded</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.15</td>
<td>0.759</td>
<td>4.67</td>
<td>0.92</td>
<td>0.85</td>
<td>2.79</td>
</tr>
<tr>
<td>16.5</td>
<td>0.444</td>
<td>7.33</td>
<td>2.00</td>
<td>1.18</td>
<td>2.10</td>
</tr>
<tr>
<td>30.2</td>
<td>0.407</td>
<td>12.3</td>
<td>2.27</td>
<td>1.61</td>
<td>2.12</td>
</tr>
<tr>
<td>46.3</td>
<td>0.287</td>
<td>13.3</td>
<td>2.82</td>
<td>2.12</td>
<td>1.69</td>
</tr>
<tr>
<td>60.3</td>
<td>0.190</td>
<td>11.5</td>
<td>4.04</td>
<td>2.56</td>
<td>1.48</td>
</tr>
</tbody>
</table>
Effect of Oxygen Content

Oxygen is an electron acceptor. Larson et al.\[25\] found that oxygen was important for the complete oxidation of 2-propanol in UV/TiO\(_2\) system. The conversion of acetone increased from 20% to 70% at illuminating 6 min with increasing the oxygen content from 0% to 5%(v/v). Figure 4 presents that \(k_{\text{app}}\) increased with increasing the oxygen content from 0% to 20% when temperature was 138°C, water vapor was 18.7 µM, and acetone was 11.4 µM. When O\(_2\) concentration was almost 0%, the photocatalytic oxidation of acetone could take place but \(k_{\text{app}}\) was small. The \(k_{\text{app}}\) was raised slowly when the oxygen content was higher than 10%. El-Maazawi et al.\[27\] proposed TiO\(_2\) lattice oxygen contributed to the photocatalytic oxidation in the absence of O\(_2\). The probability for recombination of electron/hole pairs could be reduced because gas phase oxygen adsorbed on the surface to react with electrons forming super-oxide ions (O\(_{2^-}\); Eq. (3), (4)).\[28\] Additionally, super-oxide ions are highly reactive species that can oxidize acetone. The adsorbed O\(_2\) on the TiO\(_2\) surface increases with increasing gas phase oxygen. Consequently, increasing O\(_2\) content can promote the photocatalytic oxidation of acetone. However, the surface site was saturated with adsorbed O\(_2\) when O\(_2\) content was high. Increasing gas phase oxygen did not increase the amount of adsorbed O\(_2\). Since increasing O\(_2\) content cannot accelerate the oxidation of acetone as much as low O\(_2\) content.

\[
\text{TiO}_2 + h\gamma \rightarrow h^+ + e^- \quad \text{(3)}
\]
\[
\text{O}_{2(\text{ads})} + e^- \rightarrow \text{O}_{2^-(\text{ads})} \quad \text{(4)}
\]

Effect of Water Vapor

Actually, the treatment of gaseous acetone is likely to be performed in the presence of water vapor. Influence of water vapor on the photooxidation is complex.
since water plays an important role in the formation of the active species (OH, Eq. (5)). In order to examine the effect of water vapor, different amount of water vapor were applied to a fixed concentration of acetone. Figure 5 shows the $k_{app}$ vs. initial water vapor concentration varying from 18.7 to 813 $\mu$M. The photocatalytic degradation rate was enhanced by water vapor with concentrations up to 417 $\mu$M, and inhibited above 417 $\mu$M. Acetone reacting with surface hydroxyl radicals during the oxidation process caused the depletion of these hydroxyl radicals. The presence of water vapor made the catalyst surface for rehydroxylation, increasing catalytic activity.\[18\] The oxidation rate of acetone was raised because the production of hydroxyl radical increased with increasing water vapor. Additionally, water vapor competed with acetone for adsorptive sites on catalyst surface.\[23\] At high water vapor is beneficial to adsorption of water. Therefore, the oxidation rate of acetone was decrease at high water vapor.

$$h^+ + H_2O_{ads} \rightarrow OH^*_{ads} + H^+$$

(5)

**Effect of Temperature**

Vorontsov et al.\[8\] observed temperature deactivation of TiO$_2$ for acetone oxidation in the flow-circulating reactor. Oxidation was quick as temperature increased to 100$^\circ$C, but was slow down at higher temperature. Zorn et al.\[18\] reported that the reaction rate constant of acetone significantly increased with increasing the reaction temperature from 30 to 77$^\circ$C. The temperature affects strongly the photocatalytic oxidation of acetone. Therefore, experiments involving the influence of temperature in the range from 50 to 200$^\circ$C were conducted. Figure 6 shows the $k_{app}$ of acetone oxidation increasing from 50 to 100$^\circ$C. Above 100$^\circ$C, the $k_{app}$ decreased with increasing temperature. In addition, the mineralization of acetone decreased at
high temperature. If one mole of acetone is completely oxidized, three moles of CO₂ are produced (Eq. (6)). In this study, the production of CO₂ is 2.5 mol per mole decayed acetone at 50°C, and one mole per mole decayed acetone at 200°C.

Desorption of the products from the catalyst surface is the rate limiting step at low temperature, raising the temperature accelerates the rate of desorption. It caused $k_{app}$ increasing from 50 to 100°C. Adsorption of the reactants was the rate limiting step at high temperature. Raising the temperature reduced the rate of adsorption. In addition, the catalyst was deactivated at high temperature. Hence the $k_{app}$ decreased if temperature was higher than 100°C.

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O$$  \hspace{1cm} (6)

**Kinetics**

Peral and Ollis\textsuperscript{[10]} indicated the initial rate of reaction could be described by the Langmuir–Hinshelwood kinetic rate mechanism. On the assumption of no competition with reaction by-products, the simplest representation for the rates of the disappearance of acetone is given

$$r = \frac{-dC}{dt} = \frac{k_rKC}{1 + KC}$$  \hspace{1cm} (7)

where $k_r$ is the specific reaction rate constant, and $K$ is the equilibrium adsorption constant.

A standard means of using this equation is to demonstrate linearity of the data when it is plotted as the inverse initial rate vs. initial concentration (Eq. (8)). As shown in Fig. 7, the plot of the reciprocal initial rate as a function of the reciprocal initial concentration yields a straight line. The linear transform of this
expression yields $k_r = 15.8 \mu\text{M/min}$ and $K = 0.0671 \text{L/\muM}$ ($r = 0.978$).

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r K} \times \frac{1}{C}$$ \hspace{1cm} (8)

The integrated form of Eq. (7) is

$$t = \frac{1}{k_r K} \ln \frac{C}{C_0} + \frac{1}{k_r} (C_0 - C)$$ \hspace{1cm} (9)

where $C_0$ is the initial concentration of acetone, and $t$ is the reaction time. When $C/C_0 = 0.5$, $t_{1/2}$, the half-life that does not consider the competence of intermediates, can be obtained:

$$t_{1/2} = \frac{\ln 2}{k_r K} + \frac{0.5C_0}{k_r}$$ \hspace{1cm} (10)

By substituting $k_r$ and $K$ into Eq. (10), the estimated half-lives are listed in Table 1. Figure 8 indicated the dependence of $t_{1/2}$ and $t'_{1/2}$ on initial concentration of acetone. Clearly, the difference between $t_{1/2}$ and $t'_{1/2}$ become larger with increasing initial acetone concentration. It was suggested that the reaction by-products competed with acetone so that delay the half-life. Figure 9 can assist the hypothesis. The degraded acetone almost turned into CO$_2$ at low initial concentration. Only a half of degraded acetone became to CO$_2$ at high initial concentration. Table 1 showed the ratios of CO$_2$ production to acetone degradation; they were 2.8 and 1.5 at 6.15 \muM and 60.3 \muM, respectively. Thus, the effect of by-product on the reaction rate should be considered.
In such a case, Eq. (7) may be modified to give the equation,

\[
\frac{dr}{dt} = \frac{k_r K C}{1 + K C + \sum_{i=1}^{n} K_i I_i}
\]

where \(K_i\) is the equilibrium adsorption constants of the \(i\) reaction product, and \(I_i\) is the concentration of the \(i\) reaction product. Integration of Eq. (11) yields:

\[
t = \frac{1 + \sum_{i=1}^{n} K_i I_i}{k_r K} \left[ \ln \frac{C_0}{C} + \frac{K(C_0 - C)}{1 + \sum_{i=1}^{n} K_i I_i} \right]
\]
when $C = 0.5 C_0$, $t_{1/2}$ gives
\[
t_{1/2} = \frac{0.5C_0}{k_r} + \frac{\ln 2}{k_r K} + \frac{\ln 2 \sum_{i=1}^{n} K_i I_i}{k_r K}
\]

$\frac{t_0}{t_{1/2}} = 2$ is the half-life that considered the competence of intermediates.

Theoretically, the quantity of $t_{1/2}$ modified with the effect of competition should approximate to those of $t_{1/2}$ observed in the reactions. Comparing Eq. (10) and Eq. (13), the different, $(\ln 2 \sum_{i=1}^{n} K_i I_i)/k_r K$, between $t_{1/2}$ and $t_{1/2}$ is found. By assuming that the rate of by-product formation is directly proportional to the initial concentration, it can be realized that there showed no evidence of significant difference between $t_{1/2}$ and $t_{1/2}$ at lower initial concentration and a consequence of obvious variation at high initial concentration. Xu and Raftery\([22]\) showed that the surface intermediates of photocatalytic oxidation of acetone included diacetone alcohol, mesityl oxide, formic acid, propylene oxide, and acetic acid. The half-life of acetone was extended by these intermediates competing with acetone for the oxidation. The extension time of these intermediates was shown at $(\ln 2 \sum_{i=1}^{n} K_i I_i)/k_r K$.

CONCLUSION

When the initial concentration is higher, the rate of degradation becomes fast. The photocatalytic decomposition reaction follows a first-order expression up to an initial acetone concentration. This is evidence of the straight line relationship between $-\ln(C/C_0)$ vs. irradiation time, and the slope is the apparent constant. The oxidation rate of acetone increased with increasing oxygen content from 0 to 20%. The photocatalytic oxidation of acetone can take place without the presence of gas-phase molecular oxygen. The water vapor enhanced the degradation of acetone at low and middle humidity but inhibits it at high water content. The apparent rate constant and mineralization of acetone decreased when temperature was higher than 138°C. Langmuir–Hinshelwood type behavior can be used to describe the photodegradation reaction; the reaction rate constant and adsorption constant are 15.8 μM/min and 0.0671 L/μM, respectively.

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